

Phytoremediation of Contaminated Agricultural Soil by Lead from Traffic Pollution Using a Common Barley *Hordeum Vulgare*

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Abstract

The present work aimed at studying the possibility of decontaminating polluted soil by lead from traffic road, using *Hordeum vulgare* as a heavy metals hyperaccumulative plant. High concentrations of lead stored at the horizons of soil surface (1714.39 ± 512.62 ppm) have revealed that the traffic and road infrastructures are important outcomes of toxic heavy metals to the environment. In addition, we noticed that *Hordeum vulgare* may hold a total of 36.28 ± 14.90 ppm, which correspond to 2% of that to 20% of that accumulated in the soil. Importantly, highest values were observed in the roots (18.32 ± 8.38 ppm), which means 50, 50%, whereas, the rate of heavy metals in the stems and leaves were 10.83 ± 5.86 ppm (29,95%) and 7.71 ± 3.74 ppm (21,25%), respectively. Otherwise, the accumulation of lead was influenced by physical and chemical properties of the soil (pH, cation-exchange capacity CEC, percentage of clay). A high content of lead was observed in the plant at low pH; in contrast, the CEC of the soil and the percentage of clay, positively correlated with plant Pb. However, a strong correlation between soil Pb and plant Pb was noticed. Accordingly, lead uptake by *Hordeum vulgare* seems to be influenced by its bioavailability in soil.

Keywords

Soil Pollution; Phytoremediation; *Hordeum vulgare*; Lead; Bioavailability; Algeria.

Introduction

Heavy metals, found as trace in natural soils and including their sources is lissivage by rain and the case of multiple contaminants (Rial.O et al 2003). The heavy metals can reach very high concentrations in certain substrates polluted by human activities such as the mobility of agrochemicals in soils plays an important role in the fate and transport of contaminants in the

environment (M. Pateiro-Moure and al,2010). Particularly, zinc, lead, cadmium and copper are present in emissions of different industrial and agricultural activities and are also emitted by the exhaust fumes of motor vehicles. High rates in soils could modify considerably the composition of the flora; consequently few species might tolerate their toxicity. According to Martirelli, (1999), the main sources of lead are: exhaust fumes and brake linings. The lead is deposited on the pavements and is conveyed by the storm water runoff, resulting in significant contamination of these waters.

Pagotto (1999) reported that the levels of trace metals decrease sharply with soil depth. parallel the results shown by Bermúdez-Couso.A et al. (2011) who worked on the cadofun and they say carbofuran is moderately persistent in soils, where it has a half-life of 30 to 117 days depending on the particular agri-environment conditions (soil organic matter and moisture, for example content and pH), so it is highly mobile in soil and can easily reach waters by virtue of its high solubility. As a result, carbofuran high potential for contamination of groundwater in aquifers, which it can penetrate through leaching and runoff from treated fields. As well all pesticides in groundwater and most residues present in surface water enter via the soil (Arias-Estévez et al., 2008). There are two main routes by which pesticides enter the soil: spray drift to soil during foliage treatment plus wash-off from treated foliage (Rial-Otero et al., 2003) and release from granulates applied directly to the soil (L'opez-P'erez et al., 2006). It is of paramount importance to study the dynamics of pesticides in soil-

sorption-desorption, transport (and the dependence of transport on entry dynamics and transformation processes (R. M. Gonza' et al., 2011). Indeed, it is well known that lead is generally more abundant at the surface humus horizons than in deeper horizons, nevertheless it is greatly enhanced by anthropogenic contaminations reaching the ground by its surface (Baize, 1997). According to Doelman and al (1979), soils are not the final trap for this element because when changes in physico-chemical conditions of the environment occur, lead can be remobilized by various mechanisms resulting in its migration to ground-water, contaminating water resource or assimilation by plants. Moreover, McBride (1994) showed that metal particles deposited at the surface of leaves do not enter inside and can be easily washed by rain. On the other hand, pollutants are in a soluble form usable (bioavailable) by the plant, once absorbed by the roots they can reach the aerial parts.

The use of physico-chemical techniques for the restoration of polluted soils is very hard and expensive task. Recently, more and more studies are conducted on the rehabilitation of soils contaminated with heavy metals. The ability of some plants to tolerate or even to accumulate metals has opened new area of research on soil treatment dealing on phytoremediation. Phytoremediation is both effective and low cost. It is a new technology used in the last decade for the decontamination of polluted soils, groundwater and wastewater. It is defined as the use of green plants (including grasses, herbaceous and woody) capacity to remove, contain, or render environmental contaminants harmless, such as heavy metals, trace elements, organic compounds and radioactive compounds found in soil or water. Morel (1997) reported that barley, sunflower, dandelion, various Cruciferae, nettle and rapeseed were important heavy metals hyper-accumulative plants. These plants are capable, due to their adapted physiologies, to accumulate up to 1% of their dry matter in heavy metal, which is a rate much higher than normal.

Therefore, this work aimed to use barley herb, as a hyper-accumulating plant, to clean an agricultural soil contaminated by lead from traffic road. The goal is an estimation of the concentration of accumulated lead by *Hordeum vulgare* in the vicinity of a national road with

a high traffic pressure in the region of Tiaret (Western Algeria).

Material and methods

Selection of Sampling Sites

The study was conducted in the region of Tiaret which is located in northwest of Algeria between the Tellian chain on the north and Atlassienne chain on the south, at an average altitude of 980 m. The climate type is Mediterranean semiarid with an average annual rainfall of 400 mm/year. The prevailing winds come from the west and northwest, their average speeds range from 3 to 4 m/s. The locality of Tiaret comprises over 200 km of urban road networks. In 2008, the car fleet of Tiaret department consisted of 8015 registered vehicles. This park is highly heterogeneous due to the variety of vehicles that are present (individual or utility vehicles, petrol or diesel, recent or old, etc.). New cars (0 to 5 years) represent only 11% of the park, however, the cars over 11 years account for 74%. Yet, it is precisely those older vehicles that are more polluting. (Maatoug and al, 2007).

Sampling

Initially, 20 surface horizons were chosen from Soils located near two national roads (national roads No. 14 and No. 23) to determine the levels of lead, considering that the lead is regarded as an element with a very low mobility and a strong tendency to accumulate at surface horizons (Fernandez and al. 2006). It is important to note that the daily traffic recorded on Road N°. 14 and N°. 23 is 600 and 800 vehicles per day respectively (Amirat and al, 2008). During the second year, 20 plants of common barley *Hordeum vulgare* were harvested at the same points (horizons) of soil sampling. These heavy metals hyperaccumulator and tolerant species, producing a large biomass, offer a useful alternative method in decontaminating polluted soils (Nguyen, 2007). Three plants control of common barley at nearly 5km distance from contaminated soil have been used and will serve as references when comparing to the contaminated plants in the same ecological conditions.

Treatment of samples

The preparation and analysis of metals in soil are the same as for the leaves, lichens and fungi (Flückiger

and al, 1978; Deletraz and Paul, 1998). Case of soil samples 20 soil samples were collected in each point of the study area, near the road at a distance of 2 and 4 m. The first set consists of 10 horizons at a distance of 2m from the pavement, whereas, the second set, parallel to the first, is at a distance of 4m.

Protocol

Samples were air dried, sieved (<2 mm) and then grounded. Physicochemical parameters of soil, including pH, CEC and particle size were determined by standard methods (Duchaufour, 2001). The determination of lead in soil consists to weigh 0.5g of soil and put them in glass crucibles; a passage in an oven at 105 °C for 2 hours is necessary to obtain the dry state. The samples are then calcined at 450 °C in the oven for 3 hours and the dissolution is obtained from a mixture of 10ml of 40% hydrofluoric acid (HF), 3 ml of 70% perchloric acid (HClO₄) and soil samples; the mixture is then evaporated on a hot plate at 160 °C. The fine powder obtained is dissolved with 1 ml 65% nitric acid in vials of 100 ml graduated polypropylene; after an incubation of 24 h, the tubes are boiled in a water bath and supplemented with distilled water (Certu, 2004)

Case of Plant Samples

On the same sampling points as of the soil, samples of *Hordeum vulgare* were collected (three plants per horizon) during the second year before seed formation (in April). The harvested plants required a preliminary washing with distilled water to remove possible atmospheric deposits and were separated into three organs: roots, stems and leaves. They were subjected to a set of operations:

- dehydration of organs (roots, stems and leaves): the usual method is dehydration in an oven at 105 ± 2 °C for 72 hours. The dehydrated organs were weighed separately to have the dry matter DM, which is 0.2 to 0.3 g.
- Grinding: this step is highly critical as it can be a source of contamination or loss. For this, the grinder used is an agate mortar. The grinder was Mineralization and dissolution: the fine powder obtained after calcination, was placed in an acid and oxidizing solution (0.5 ml mixture of nitric acid HNO₃, hydrofluoric acid HF and perchloric acid ClHO₄) and then heated in a water bath for 24 h until the complete destruction of organic matter. Tubes that have been

put to boiling were supplemented with 10 ml distilled water. This method allows the determination of the set of mineral trace elements (Certu, 2004).

Quality Control and Assurance

For the determination of lead by atomic absorption spectrometer (whose characteristics are: analytical line: 283.3 nm, slit width: 0.5 nm, correction system: Zeeman effect, systematic addition of 5 ul of diluted modifier matrix 1/5), the detection limit was 0.2 ug /g and the limit of quantification is 0.3 mg /g with a standard deviation of the blanks estimated at 0.2 ug /g (Chiffolleau and al., 2003). The standard solution used in this experiment is the PbCl₂ (10 mg / l) and the calibration curve was plotted according to the values: 0.5, 2.0, 5.0, 10.0; 20.0 µg/ml.

Initial control measurements include three assays performed, the coefficient of variation is 14.4% as the maximum value. The mean average is used as the midpoint of the diagram and alert thresholds are set to + 2 and -3 from standard deviations. On the basis of a normal repeat, 95% average measurements of later series should be within the range of +2 and -2 from standard deviations (0.00049 ± 0.02088 percentage Mass.).

Results and Discussion

Lead Levels in the Plant and Soil

All results are presented in (Table 1) which summarizes the different concentrations of lead absorbed by *Hordeum vulgare*, in the three organs (roots, leaves and stems), as well as the levels of lead in soil bordering the pavements of the two roads concerned by this study.

Data from table 1, reveal a strong contamination of the soil by lead (1714.39 ± 512.62 ppm) with a remarkable variability between different sampling points; hence the recorded values of lead in the plant *Hordeum vulgare* (36.28 ± 14.90 ppm) greatly exceeded the control values (2.58 ± 0.16 ppm) and standard values (1.38 ± 1.24 ppm) (according to Baize, 1997). Larger values were observed in the roots (18.32 ± 8.38 ppm), concentrations were lower in stems and leaves whose recorded values were respectively: 10.83 ± 5.86 ppm and 7.71 ± 3.74 ppm. Lead is mainly absorbed by root hairs and stored in the cell walls, which explains the high rates in roots (Hughes and al., 1980). However,

TABLE 1 DESCRIPTIVE STATISTICS ON LEVELS OF LEAD (PPM) IN THE PLANT AND SOIL

		N	Mean	Median	Min	Max	1er Q	3ème Q	S.D
Roots		20	18,32	15,75	7,00	30,90	11,25	27,75	8,38
Stems		20	10,83	8,55	4,10	28,50	6,85	15,15	5,86
Leaves		20	7,71	6,90	1,10	16,70	5,50	10,26	3,74
total		20	36,28	33,52	13,70	71,20	24,50	47,48	14,90
witness	Roots	03	1,17	1,20	1,13	1,20	1,13	1,20	0,04
	Stems	03	0,83	0,84	0,70	0,97	0,70	0,97	0,13
	Leaves	03	0,57	0,56	0,50	0,65	0,50	0,65	0,07
	total	03	2,58	2,62	2,40	2,73	2,40	2,73	0,16
Norms (plants)		5	1,38	-	0,01	2,50	-	-	1,24
Soil		20	1714,3 9	1688,17	845,6 0	2712,0 0	1326,3 0	2082,00	512,62
(soil not contaminated)		-	9 – 50 100	-	-	-	-	-	-

Contat and al,1991) found much more Pb in the 0-20 cm layer than in deeper soil layers, where the roots are more abundant. Jean (2007) found that the presence of metals in different parts of the plant indicates that there is an accumulation but also a translocation to aerial parts. Several researchers have demonstrated the possibility of using plants for remediation of soils contaminated by trace metals. However, in the case of soils contaminated by heavy metals, it is admitted that a relatively large proportion of Cu, for example, can accumulate in the roots without an increase of the concentration in aerial parts Martirneli (1999).

Therefore, the assessment of bioavailability of Cu concentrations by analysing the roots in addition to the aerial parts is more relevant lead reacts with organic acids in soil solution according to The following reactions (Marie. 2008):



With R-COOH: carboxylic acid, R-OH alcohol or phenol (organic ligands).

Moreover; Kabata and Alina (2001) found that the lead threshold values of plants grown in non-contaminated areas, ranged from 0.05 to 3.0 mg g⁻¹ during the period 1970 to 1980, while the average lead content for cereals from different countries appeared to vary considerably from 0.01 to 2.28 mg g⁻¹, in contrast, it was 2.1µg g⁻¹ in the forages and 2.5µg g⁻¹ for grasses.

Effect of Soil Physicochemical Factors on Lead Absorption by the Plant

The transfer of Pb to the plant is certainly conditioned by the physicochemical parameters of soil, including pH, CEC, rate of clay and the plant itself. Similar results are shown by Pose-Juan .E and al. (2010) for metalaxyl, they found that The amount of dissolved metalaxyl depends mainly on the interaction of three factors: soil pH, its potential acidity, and the cation exchange capacity. The surfactants and soil have a synergic effect on the overall retention of metalaxyl. This should be considered in the estimation of metalaxyl mobility in agricultural soils.

Effect of Soil pH

This correlation is illustrated in Figure.1, where a negative relationship is observed; with a correlation coefficient $r = - 0.49^{**}$. Furthermore, analysis of variance indicated a significant effect of pH on plant's lead ($p < 0.01$).

It was observed that at low pH, metal cations are more available for absorption by the plant. Different interpretations have been advanced to explain the influence of soil pH on the accumulation of lead. McBride (1994) found that Cd, Cu, Hg, Ni, Pb and Zn are strongly absorbed by the roots at pH <5.5, so it is possible to increase the phytoextraction by adding an acidic agent to a contaminated soil.

On a physiological level (Hisinger, 2001) noted that the pH can be modified by the exchange activity of roots: to maintain electrical neutrality, the plant has a compensating effect of ion uptake by a charge release at root level. When they take more cations than anions, roots compensate by releasing in the rhizosphere an excess of positive charges in the form of protons, resulting in acidification of the environment. Jean.L (2007) showed that the increase in pH favors protons elimination from aqueous complexes and surface functional groups of the solid phases. Due to the decrease of protons, competition between protons and metal cations is lower and therefore repulsions are decreased which.

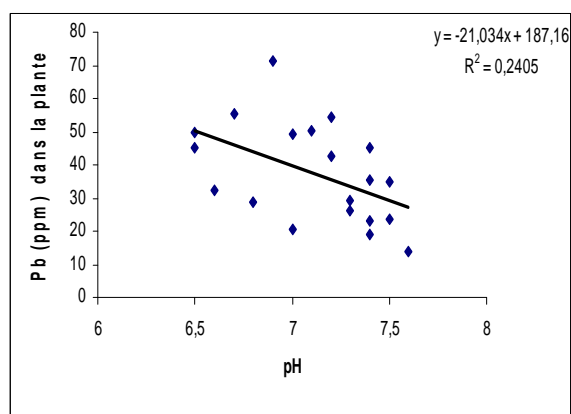


FIG .1.CORRELATION BETWEEN THE PH OF THE RHIZOSPHERE AND THE ACCUMULATION OF LEAD IN HORDEUM VULGARE

then accelerates the formation of new phases. Thus, the solubility of metal cations decreases with increasing pH. For the plant to maintain an electrostatic equilibrium and a constant pH in root cells; cation samples are exactly compensated by the release of H^+ ions or the removal of anions; in contrast, the anion samples are compensated by the release of OH^- , HCO_3^- ions or by the removal of cations (Straczek, 2003).

Effect of CEC

The cation exchange capacity of soil is positively correlated with concentrations of lead in the plant ($r = 0.52^{**}$) as shown in Figure 2. The Anova revealed a significant effect of this parameter ($p < 0.01$).

The cation exchange capacity is interdependent and determines much of the retained amounts of pollutants, including adsorption of pollutants that can be represented by the CEC, which is the maximum amount of cations that the soil can hold by physico-chemical adsorption. However, the root cation exchange capacity (CECr) is defined as the number of

binding sites for cations (anionic groups) localized on the cell walls. The increase in CEC gives to soil a chance for longer fertility. The CEC increase is also important for contaminants retention (M. Pateiro-Moure et al.2009). Likewise M. Pateiro-Moure et al.2008 found that the ratios of the variables measured between soil deposits and soils, it was found a significant correlation between the increase of PQ in soil deposits and their increase in CEC ($r = 0.826$, $p = 0.43$, $n = 6$).

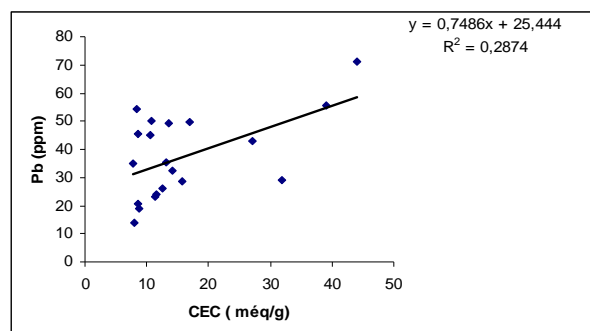


FIG .2. CORRELATION BETWEEN THE CATION EXCHANGE CAPACITY AND THE ACCUMULATION OF LEAD IN HORDEUM VULGARE

These ions can then accumulate in the rhizosphere and lead in calcareous soils to precipitates of calcium carbonate around the roots (Jaillard,1985). Conversely, the elements present in small amounts in the soil solution, as is typically the case of trace metals (Pb, Zn, Cd, etc. ...), are also transferred by the mass flux, but is insufficient compared to the removal of the plant (Hisinger and al,2001).

This therefore leads to a decrease in the concentration of metals such as Zn and Cd in soil solution near the roots (Lorenz and al, 1994). This reduction creates a concentration gradient between the soil (mineral, soil solution) and roots and a diffusive transfer of these elements to the roots. (Mico and al, 2008) investigated the accumulation of Co in *Hordeum vulgare* growing in a soil contaminated by this element.

The results showed a significant correlation ($r = 0.98$) between the contamination of the plant and increasing soil CEC; in contrast, no relationship between this contamination and organic carbon was found.

Effect of clays

Recall that the clays are characterized by a non-neutral electrical surface, which determines their ability to exchange ions. These minerals have two

types of charge. The first, a negative charge, is structural and can not be changed. It is linked to Al^{3+} , Si^{4+} or Mg^{2+} , Fe^{2+} , Al^{3+} substitutions, in the layers of clay. The second, related to chemical reactions that occur on the surface of minerals, is a surface charge variable depending on the pH of the medium. For a low pH, the majority of H^+ ions bind to clay more than the OH^- . The result is an overall positive charge and the clay is characterized by an anion exchange capacity. For high pH, the dominant OH^- lead to an opposite phenomenon, and clay develops a CEC.

A positive relationship exists between lead absorption by the plant, and the rate of clays; the more this rate is important, more the CEC is important, more the plant has a high accumulative power. Figure. 3 shows this relationship ($r = 0.80^{**}$). Analysis of variance showed a highly significant effect on the correlation ($p < 0.01$). lead on the biological processes of the plant, such as photosynthesis, mitosis and water absorption, but rapidly converted into lead compounds soluble in water, easily available to plants.

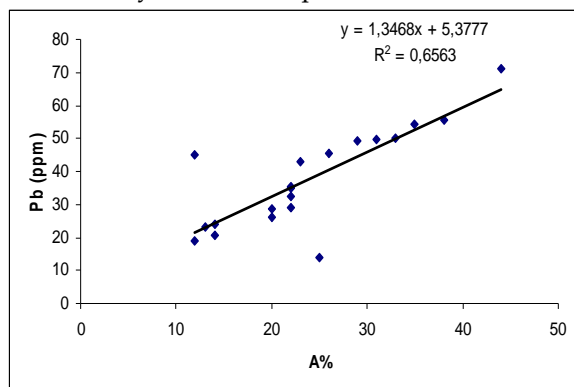


FIG. 3. CORRELATION BETWEEN THE RATE OF CLAY (%) AND ACCUMULATION OF LEAD IN *HORDEUM VULGARE*

Indeed, the higher the clay, the higher the CEC and the higher the plant absorbs metal; in this case, lead transfer to the plant is passive. Organic matter and clays play an important role in the adsorption of lead by the plant. The trace elements show a high affinity for humic substances with which they form stable humic clay complexes, possibly soluble. This explains the abundance of trace elements on the surface especially in the presence of organic matter where trace elements are absorbed specifically by iron oxides and manganese oxides (Baize, 1997).

Correlation: Pb Plant- Pb soil

The correlation Pb plant - Pb soil is shown in Figure.4. This highly significant correlation ($r = 0.72^{**}$)

may explain the high bioavailability of Pb to be taken by the plant (particularly by roots). The more the lead is bioavailable in the soil; the more it is easily absorbed by the plant. The best accumulation was recorded in the roots ($r = 0.72$).

In the case of *Hordeum vulgare*, (Figure. 5) shows that about 2% of lead in soil is absorbed by the plant, without any phytotoxic symptoms. In this case, several studies describe the toxic effects of Doelman and Haanstra (1979) have shown that the accumulation of lead in surface soils has a great ecological importance because this metal is known to affect greatly the biological activity of soil which means its absorption by plants. The soil is a reservoir of metals for plants. This leads to consider that the totality of metals is also available for the plant. The concentrations of Cd, Zn, and Pb in the straw and wheat grain are directly dependent on those of the ground (Hagemeyer, 2004).

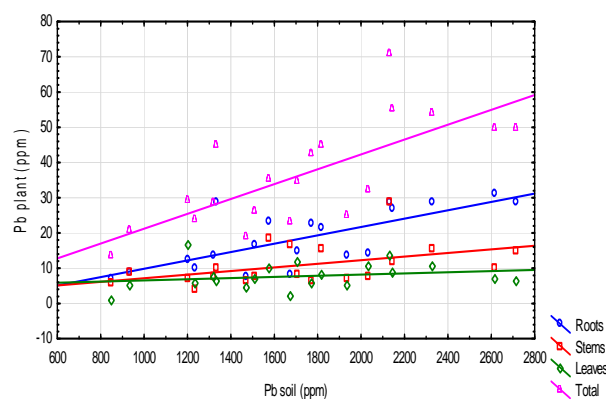


FIG. 4. CORRELATION: PB SOIL – PB PLANT (*HORDEUM VULGARE*)

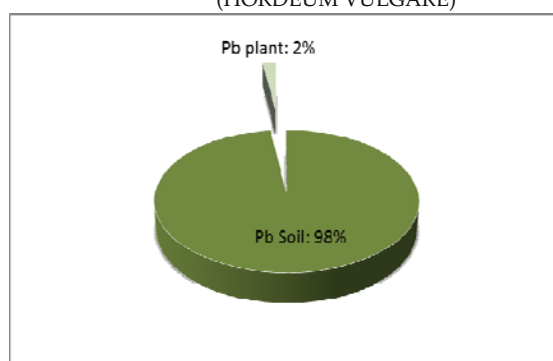


FIG 5. PERCENTAGE ACCUMULATION OF LEAD IN *HORDEUM vulgare*

Conclusion

The objective of this work was to show that the common barley *Hordeum vulgare* has the potential to effectively decontaminate soil, located near a high

pressure traffic road, contaminated with lead. The experimental protocol consisted in determining the concentrations of this metal, in 20 soil samples and 60 samples of *Hordeum vulgare* (roots, stems and leaves). The results showed that the surface horizons of road soils were highly contaminated by lead (1714.39 ± 512.62 ppm) and exceeded the international standards. However, 2% of this value can be absorbed by *Hordeum vulgare* that is 36.28 ± 14.90 ppm. Larger values were observed in roots with 18.32 ± 8.38 mg g⁻¹; while, the values observed in the stems and leaves were, respectively: 10.83 ± 5.86 pmm and $7,71 \pm 3.74$ ppm. This rate of annual accumulation remains interesting if the Algerian government sets the regulations for total halt to the sale of leaded gasoline. The plant Pb's accumulation is influenced by physicochemical parameters of soil such as soil pH, CEC and the rate of clays. At low pH, lead is available to be absorbed by the plant ($r = -0.49^{**}$) while CEC and the rate of soil clays are positively correlated with levels of lead in the plant ($r = 0.52^{**}$ and $r = 0.80^{**}$, respectively). The transfer of the lead to the plant is done passively. model the fate of pollutants from a contaminated site, to assess risks and hence choosing a remediation strategy. The effects of heavy metals on local ecosystems and the mechanisms of their transfer, from soil to plants, are still not well understood. It is therefore very difficult to predict their long-term effects, to However, plants grown for consumption are a potential hazard to public health because of a possible accumulation of these elements in their tissues. Risks associated with contaminated soils are in fact closely related to the bioavailability of the metallic elements. Once absorbed, these metallic elements can return to the soil (biogeochemical cycles). Moreover, these contaminated plants, can not and should not be used as human or animal food. Unfortunately, there is no concern whether the highly accumulative plants are used or not for certain animals and thus generating a contamination of the food chain. How to control the spread then? Research should be conducted in this area. It is at this stage that checks should be performed. Studies on these phenomena are still not developed but seem promising.

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